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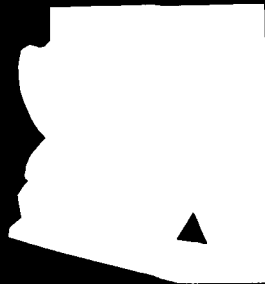
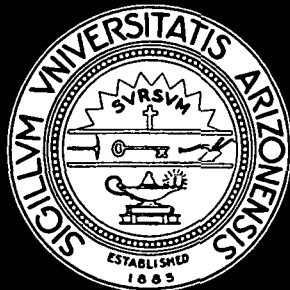
DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

Seventeenth Six-Month Report  
for the period  
1 July 1971 to 31 December 1971

For the  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
Grant NGL-03-002-019

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Field Emission and Space Systems Laboratory  
Electrical Engineering Department  
The University of Arizona  
Tucson, Arizona 85721



ENGINEERING EXPERIMENT STATION  
COLLEGE OF ENGINEERING  
THE UNIVERSITY OF ARIZONA  
TUCSON, ARIZONA

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by

Stuart A. Hoenig  
Principal Investigator

Graduate Assistants

Robert A. Goetz  
Freedoon Tamjidi  
Fred A. Moore

Undergraduate Associate

Michael R. Pomeroy

Laboratory Technician

Christian W. Savitz

Secretary

Ellen O. Nelson

Field Emission and Space Systems Laboratory  
Electrical Engineering Department  
The University of Arizona  
Tucson, Arizona 85721

## I. INTRODUCTION, ABSTRACT AND SUMMARY

This report will cover the work performed from 1 July 1971 through 31 December 1971 on Grant NGL 03-002-019 between the University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially, the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere and adsorption system for control and separation of gases.

Results to date have included detectors for  $O_2$  and  $H_2$  under partial vacuum conditions (publications 1, 3, 4). Experiments on detectors for use at high pressures began in 1966, and systems for CO,  $H_2$ , and  $O_2$ , were reported in 1967 and 1968 (publications 8, 11). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semiconductor material could be electrically cycled to adsorb and desorb a specific gas. This work was extended to obtain quantitative data on the use of semiconductors as controllable adsorbents (publications 11, 12).

In 1968 a new technique for dry replication and measurement of the thickness of thin films was developed. A commercial material, Press-O-Film was shown to be satisfactory when properly used. This technique is most useful for studies of semiconductor thin films where normal interference techniques are not practical because of the non-reflective nature of the film (publication 13).

In 1969 studies began on a corona discharge detector for water vapor. This system was shown to be rapid in response, suitable for continuous low power operation and reasonably linear in output (on a logarithmic plot) from 10% relative humidity to 75% relative humidity. A program to develop this detector for hydrological applications began in 1970. A field usable system was developed for the Hydrology Department and finished in 1971. A unique feature of this system was the fact that no fan was needed. Airflow through the system was induced by the corona discharge itself, (this is often called the Electric Wind Effects).

The electroadsorption phenomena reported in 1968 (publication 12) was extended to bulk ZnO samples by using a gas chromatograph. The objective of developing a controllable electroadsorbent is slowly being realized.

Studies of the reaction between carbon monoxide and palladium have been under way since 1966. In 1970 this work was split into two separate programs; the first is a study of gas-metal interactions with emphasis on catalysis. The second was a development of the CO/Pd system into a practical system for use by the Division of Occupational Safety and Health of the Environmental Control Administration. This system was delivered to the ECA in December 1971 and is presently being evaluated by that organization.

The catalysis studies were devoted to the oxidation of CO, H<sub>2</sub> and NH<sub>3</sub> over metallic catalysts. We demonstrated that the rate of reaction could be observed and controlled in terms of the exo-electron emission from the catalyst, (publication 16). In 1971 this study was

directed to the extended metal-ceramic catalysts used for auto exhaust emission control and for spacecraft atmospheric purification.

In 1971 we began the study of a new technique for analysis of solid materials. This system involved heating or grinding the substance and observing the induced exo-electron emission. This effect is known as Temperature Stimulated Exo-Electron Emission (TSEE) and can be used to determine the silica content of various minerals.

This technique has possible applications in the study of planetary soils picked up by landing vehicles. Another potential application exists in the Public Health area where silicosis is a serious industrial problem. There may be direct connection between the exo-electron emission we observe after grinding and the development of human silicosis.

## II. SUMMARY OF WORK IN THE PAST SIX MONTHS

### A. Carbon Monoxide Detector

This program has been supported by the Environmental Control Administration rather than NASA and will therefore be discussed in Section E (Other Activities in the Laboratory) of this report. Here we shall only comment that the detector operates at CO levels below 50 PPM. A final model of this system has been prepared, constructed and delivered to the ECA.

### B. Corona Discharge Humidity Detector

The current generated in a point-to-plane corona discharge has been shown to be dependent on the ambient water vapor pressure. The

use of a multipoint brush and an ultraviolet source stabilizes the system and maintains sensitivity over a wide range of relative humidity. The fact that airflow through the system is induced by the electric wind effect of the corona discharge makes the device quite suitable for field applications.

Our first plan for installing this device at a Hydrology field station during the Summer of 1971 was abandoned when the station was struck by lightning and destroyed. We expect to rebuild the system during the next 6 month period and install it in a field station.

### C. Surface Catalysis and Exo-Electron Emission

This program is an outgrowth of our earlier studies of gas-surface interactions with the mass spectrometer. We have shown that when catalytic oxidation of  $\text{CO}$ ,  $\text{H}_2$ , or  $\text{NH}_3$  begins (on hot platinum) there is emission of nonthermal exo-electrons. This "exo-electron" emission can be used to monitor the rate of catalysis. Suppression or enhancement of this exo-electron emission results in an increase or decrease of the rate of catalysis itself. A paper on this topic has been submitted to the Journal of Catalysis. A copy of the manuscript is attached to this report as an appendix.

In more recent work we have obtained a correlation between the relative rate of reaction and the measured exo-electron current during the oxidation of  $\text{NH}_3$ . This is shown in Figure 1, the two curves are essentially parallel until at  $770^\circ\text{C}$  thermionic emission overwhelms the exo-electron signal.

These results agree with our previous experiments which suggested that catalysis involves surface mass migration with subsequent electron emission. This mass migration occurs in a region where extensive chemisorption has occurred. The metal-gas "compound" layer formed by chemisorption is a semiconductor and might be expected to be affected by electric fields.

The final settlement of this question will require a number of years. At the moment we are redesigning the system to make use of an alumina dispersed catalyst. The initial structure will be an  $\text{Al}_2\text{O}_3$  tube which has been filled with a metal salt and then dried, (Reference 1). This will serve as a first approximation to the catalysts used in spacecraft and automotive environmental systems.

We will make electrical contact to the alumina tube by means of a conducting strip. The alumina tube will be heated by an internal nichrome filament. It will be important to determine if exo-electron emission occurs during catalysis and how it is related to the catalytic process.

#### D. Analysis of Soil Samples by Means of Exo-Electron Emission

One of the major objectives of the planetary landing experiments has been the analysis of rock and gravel type materials. Many techniques have been investigated, but a need for new instruments, of a simple type, still exists. In view of this interest in soil analysis we have been investigating the possibilities of analyzing soil samples for their silica content by heating or grinding the sample and observing the exo-electron emission. Typical results for the heating technique were

reported six months ago. Recently we have been investigating the exo-electron emission that occurs when siliceous materials are ground in a small vibratory ball mill. The experimental set-up is shown in Figure 2, the grinding media was 6 millimeter glass balls. The advantages of this system are significant, first the samples can be ground in the collection tube without the exposure to contamination and loss that occurs when the material must be transferred to the heating system. After grinding the tube, sample and glass beads can be discarded or stored for future study.

Typical results on sample *industrial* materials provided by Mr. John Crable of the Environmental Control Administration, are shown in Figure 3. There is an apparent difference in the curves which can be empirically related to the silica content. These studies are continuing, we hope to determine how this analysis technique can be used on a variety of minerals. There is reason to believe (Reference 2) that eventually we will be able to detect trace metal impurities in rock materials by an exo-electron technique.

#### E. Other Activities in the Laboratory

The ARPA-sponsored studies on the relationships between fatigue and subsequent exo-electron emission are continuing. We have shown if a metal is fatigued to some fraction of its total life and then heated gently, it will emit exo-electrons. This electron current can then be related to the fatigue history of the specimen. We have developed an exo-electron system for scanning along an aircraft structure to detect cracks or crack growth during flight.



This technique has been extended to the monitoring of stress relief annealing processes. We are considering the application of this method to post-weld heat treating of ship structures. The results to date have been submitted for publication (publication 17).

Another use of laboratory facilities occurs in connection with two courses taught by Professor Hoenig in Electronics and Instrumentation for graduate students in the Zoological, Geological and Medical Sciences. These students use the laboratory and its apparatus for demonstration and simple projects. This would be impossible without the long term support that we have received from NASA.

The laboratory is still used occasionally by members of the University of Arizona Lunar and Planetary Laboratory. We feel that this use of NASA supported facilities by another NASA funded project is an important example of how research funds can be conserved by joint use of facilities.

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#### PERSONNEL

Students who have been supported by the grant and their present activities are listed below:

1. Donald Collins, M.S., 1963; Ph.D., California Institute of Technology, September 1969. Presently Research Associate, CIT.
2. George Rozgoni, Ph.D., 1963; Senior Staff Member, Bell Telephone Laboratories, Murray Hill, New Jersey.
3. Donald Creighton, Ph.D., 1964; Professor, University of Missouri, Rolla. (Partial NSG-458 support.)
4. Lt. Col. C. W. Carlson, M.S., 1965; Active Duty, U. S. Army.
5. Melvin Eisenstadt, Ph.D., 1965; Professor of M.E., University of Puerto Rico, Mayaguez, P.R.
6. John Lane, M.S., 1968; Philco Ford Company, Tucson.
7. William Ott, M.S., 1970; Burr-Brown Research, Tucson. (Partial NASA support.)
8. Richard Pope, M.S., 1970; Hewlett-Packard Corporation, Palo Alto, California.

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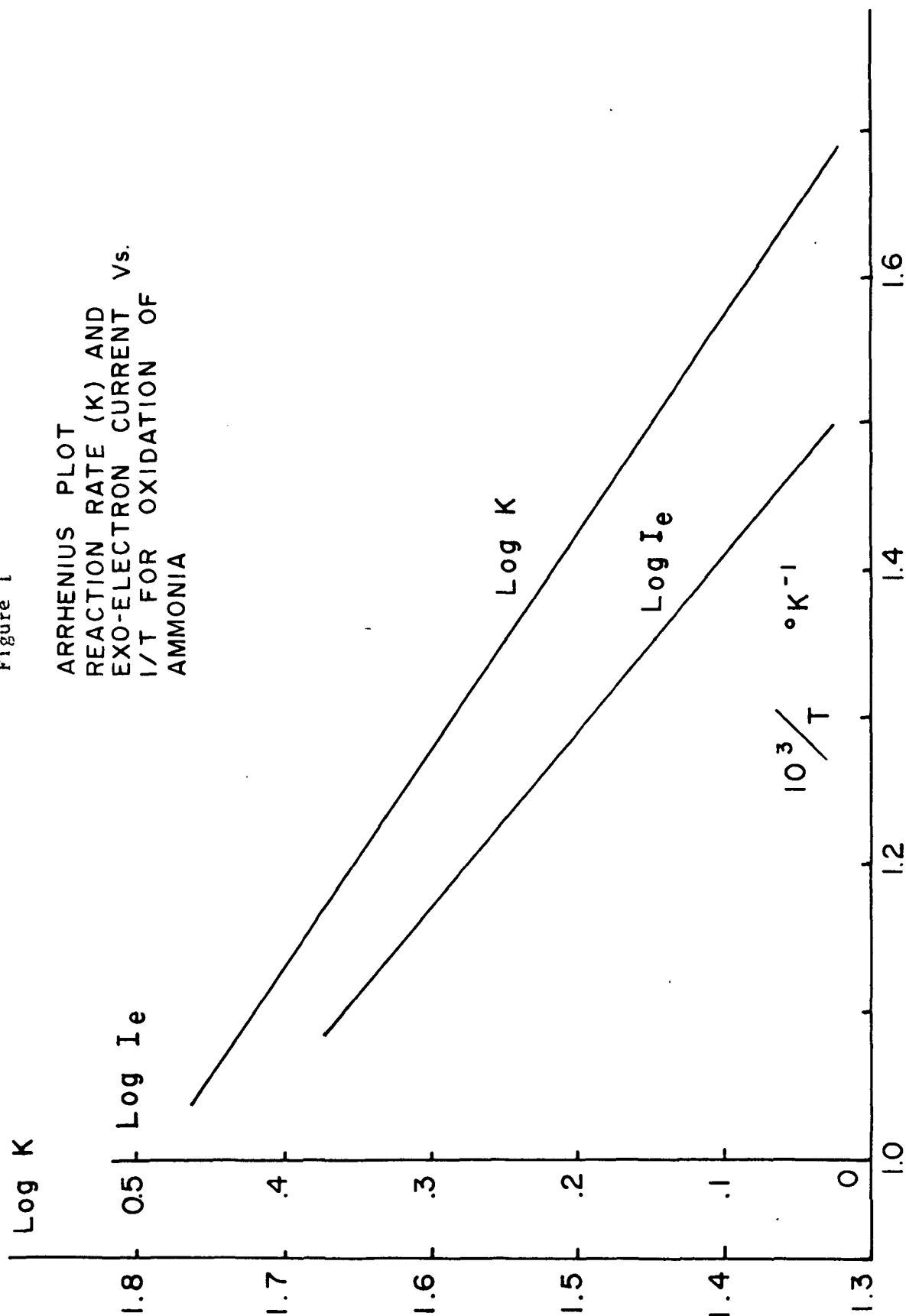
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16. "Electron Emission During Heterogeneous Catalysis (The Effect of External Electric Potentials)," Submitted to the Journal of Catalysis, with Freedoon Tamjidi.
17. "Applications of Exo-Electron Emission to Nondestructive Evaluation of Fatigue, Crack Growth, and Annealing Processes," Submitted to the Journal of The American Society for NDT, with C. W. Savitz, W. A. Ott, T. A. Russel, and M. T. Ali.

FIGURES

1. Arrhenius Plot Reaction Rate (K) and Exo-Electron Current Versus  $1/T$  for Oxidation of Ammonia.
2. Exo-Electron Grinding Test System.
3. Exo-Electron Emission Current Versus Time During Grinding of Various Siliceous Materials.

Figure 1

ARRHENIUS PLOT  
REACTION RATE (K) AND  
EXO-ELECTRON CURRENT Vs.  
 $1/T$  FOR OXIDATION OF  
AMMONIA



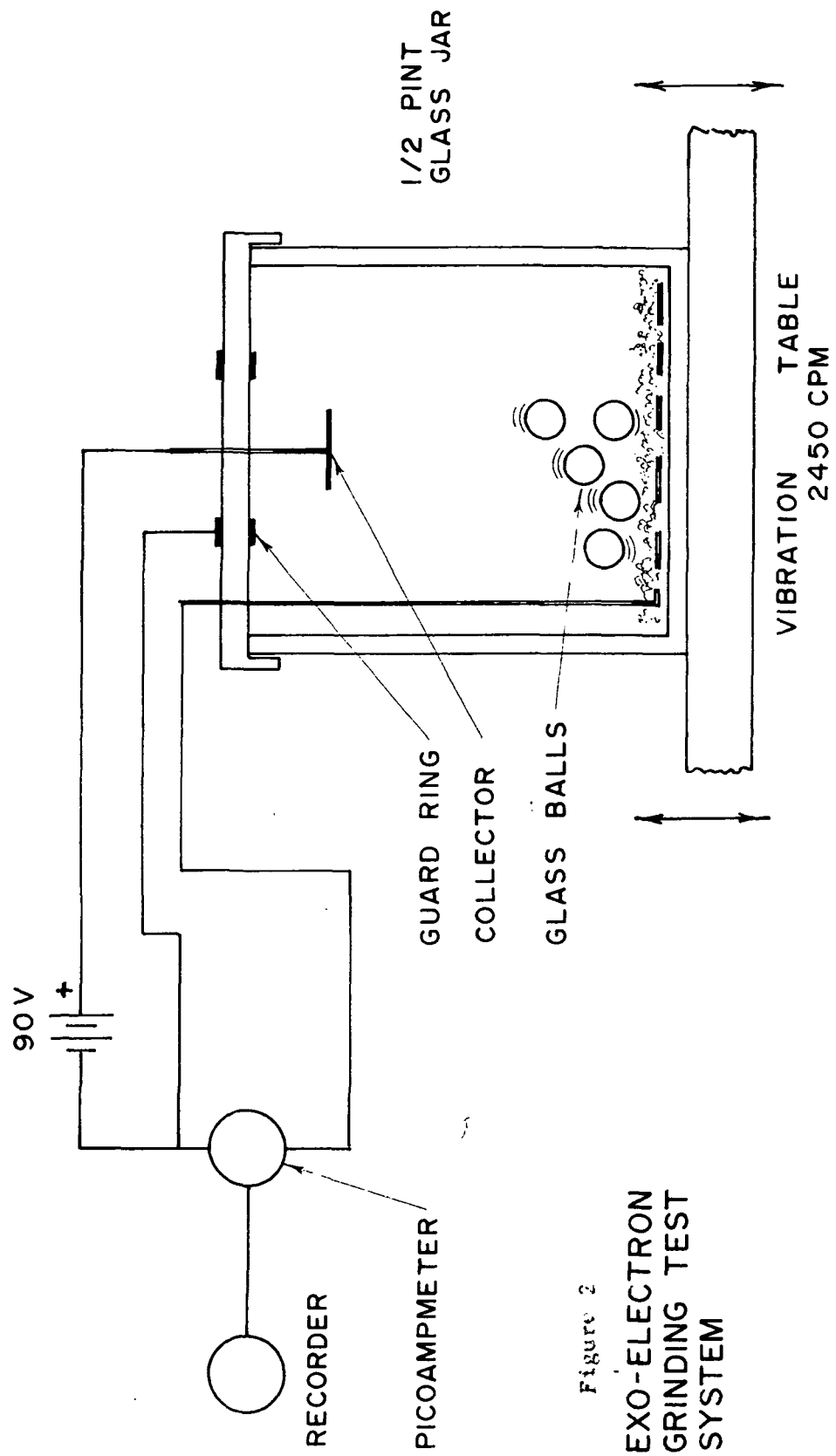
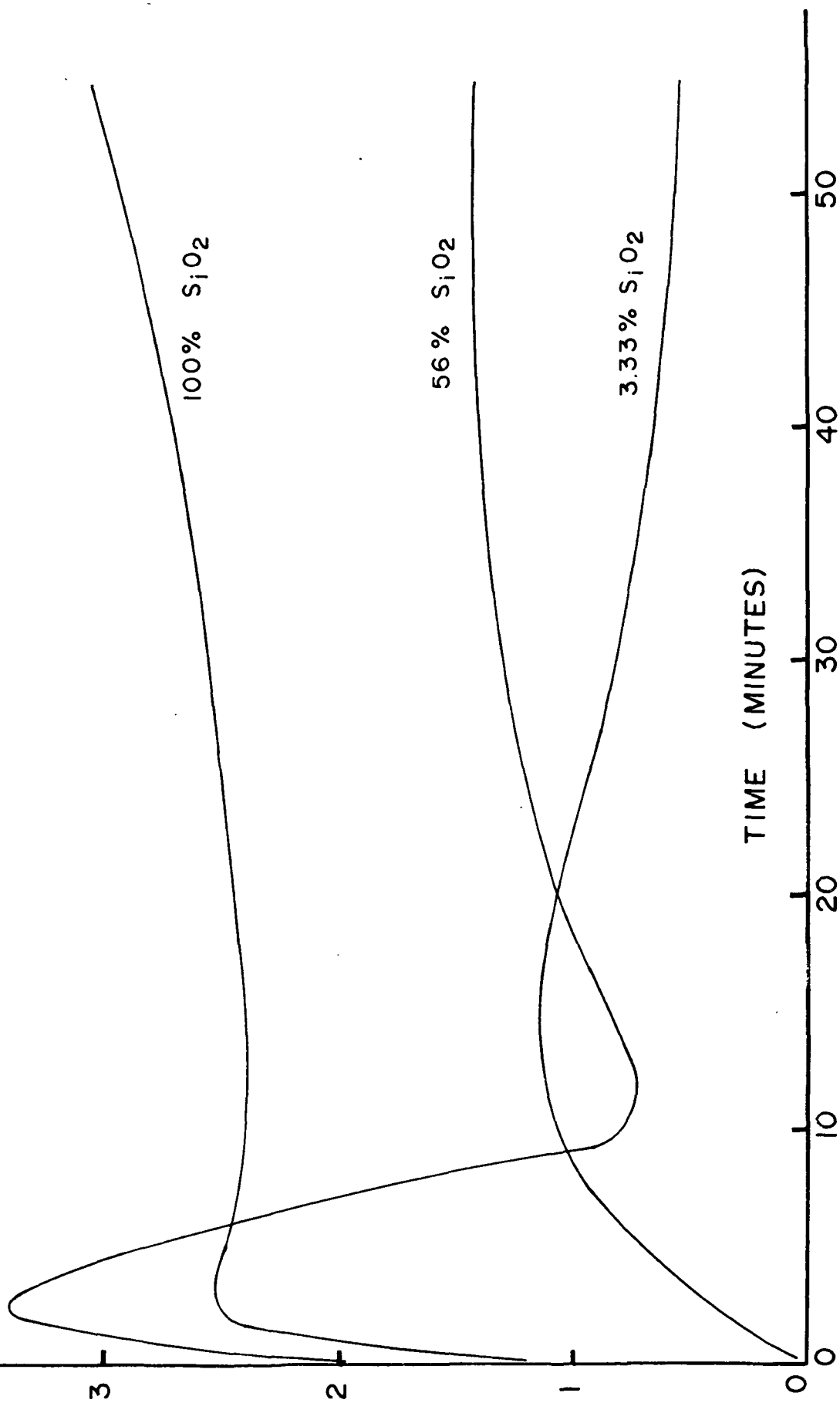


Figure 2  
EXO-ELECTRON  
GRINDING TEST  
SYSTEM

$I \times 10^{-12}$  AMPS

Figure 3

EXO-ELECTRON CURRENT Vs.  
TIME DURING GRINDING OF  
VARIOUS SILICEOUS MATERIALS



## APPENDIX

### Exo-Electron Emission During Heterogeneous Catalysis (The Effect Of External Electric Potentials)

BY

Stuart A. Hoenig and Freedoon Tamjidi  
Electrical Engineering Department  
University of Arizona, Tucson 85721



### Abstract

Exo-electron emission was observed during catalytic oxidation of CO, H<sub>2</sub> or NH<sub>3</sub> on hot platinum. The exo-electron current level was related to the rate of reaction. Suppressing or enhancing the exo-electron current decreased or increased the rate of reaction.

Exo-Electron Emission During  
Heterogeneous Catalysis  
(The Effect Of External Electric Potentials)

By

Stuart A. Hoenig and Freedoon Tamjidi  
Electrical Engineering Department  
University of Arizona, Tucson 85721

I. Introduction

The proposal that an external electric field could affect a metallic catalyst is at least 40 years old (1). In fact, effects of this type have been observed from time to time (2), but the diverse results and lack of a mechanistic explanation have hindered investigators.

Electrostatic field effects are well known in semiconductor catalysis studies and a review of this work was given in 1963 by Volkenshtein (3). The application of these principles for catalyst selection is now well known (4). The effect of electric fields on adsorption follows from the same theory and experimental evidence on ZnO was given in 1968 (5).

The observation that catalytic reactions may induce exo-electron emission was reported in 1967 and a linear relation between the rate of reaction and exo-electron emission was observed (6). Similar studies were reported in (7). In neither case was any attempt made to suppress or enhance the exo-electron current.

We suggest that many of the effects of electric fields on metallic catalysts (8, 9), may be understood in terms of exo-electron emission. It will be shown that during the adsorption phase of a

catalytic reaction, the catalyst surface is disturbed and exo-electrons are emitted. This exo-electron current may be used to follow the rate of reaction. It also appears that this electron current is somehow related to the catalytic mechanism in the sense that enhancing or suppressing the exo-electron emission, increases or decreases the rate of catalysis. These phenomena offer the opportunity for improved techniques for the monitoring and control of heterogeneous catalysis.

## II. Experimental Studies

### A. Apparatus

The system is shown in figure 1. The mass spectrometer was an EAI Quad 250 which was used to control the gas mixture in the system and to monitor product peaks during catalytic reactions. The catalysts were in the form of wires 0.25 mm in diameter. The catalyst material was commercial platinum (99.995%). The catalyst filament was heated by AC current with an isolated power supply. Filament temperatures were monitored by a welded-on thermocouple. The catalyst wires could be biased at any value from "0" (ground) to  $\pm$  900 volts by means of a Fluke Power supply. The exo-electron currents were collected by a stainless steel collector biased at +24 volts, and measured with a Keithley 417 picoammeter. The vacuum system was stainless steel, with copper gaskets, pumped to  $10^{-5}$  torr by an oil pump and to  $10^{-9}$  torr by a 50 l/s Vac-Ion pump. The oil pump was isolated from the system during the catalysis experiments. Tests to determine if the Vac-Ion pump was producing

any signals in the electron measurement system were negative.

Experimental studies were made of the catalytic oxidation of CO, NH<sub>3</sub> and H<sub>2</sub>. The gases were commercial grade taken from standard cylinders. The gas input was controlled by Granville-Phillips leak valves. Partial pressures were monitored by a discharge gauge and the Vac-Ion pump current. All oxidation experiments were run at a total pressure of  $6 \cdot 10^{-6}$  torr. The CO, H<sub>2</sub> or NH<sub>3</sub> partial pressures were held at about  $1 \cdot 10^{-6}$  torr during the experiments.

#### B. Experiments and Results

Investigation of the background effects involved grounding the filament (catalyst) and biasing the collector at +24 volts, with the vacuum system pumped to  $10^{-8}$  torr. Then each of the gases we planned to use was admitted until the system reached a pressure of about  $10^{-6}$  torr. For each gas, the platinum filament was slowly heated from 20°C to 800°C while the mass spectrometer and the picoammeter were used to look for spurious signals. No reaction products were observed, but there was some exo-electron emission due to changes in the work function of the filament induced by chemisorption and surface rearrangement. The effects are shown in figure 2. Oxygen increases the work function and hydrogen reduces it. CO and NH<sub>3</sub> reduce the emission below the vacuum level.

The first platinum catalysis studies were done with H<sub>2</sub> and O<sub>2</sub>. Here the rate of catalysis was small at room temperature but rose rapidly as the catalyst was heated to the operating temperature, 775°C. The exo-electron emission followed the rate of catalysis as shown in figure 3. Here the height of the H<sub>2</sub>O peak (K) in

arbitrary units and the exo-electron current ( $I_e$ ) in amps, are plotted as a function of time. Notice that the exo-electron current follows the rate of reaction and is somewhat erratic until (K) becomes constant, at which time  $I_e$  drops to a slightly lower level. This phenomena was quite consistent and a series of experiments at higher and lower filament temperatures indicated that the time for the drop to occur decreased with increased filament temperature. For example, at  $800^{\circ}\text{C}$  (K) reached equilibrium in 7 minutes and  $I_e$  fell to the lower level value. At  $700^{\circ}\text{C}$  a longer time (15 min) was required before (K) reached a constant value and  $I_e$  fell to the lower level.

It seems that once equilibrium is established, the situation is quite stable. Raising or lowering the catalyst temperature by  $50^{\circ}\text{C}$  did not appreciably change (K) or  $I_e$ .

In figure 4 we show similar results for oxidation of CO. The numerical values of (K) and  $I_e$  are different, but the qualitative behavior is quite similar. In figure 5 data on the catalytic oxidation of ammonia is shown. Here again the exo-electron emission follows the reaction, drops to a lower level as the rate of reaction stabilizes, and then surges as the heating current is turned off. This surge is of considerable interest and was observed whenever the catalyst was allowed to cool to  $20^{\circ}\text{C}$  from its operating temperature. We emphasize that this is not a switching transient, the time is far too long. Data to be presented below will demonstrate that the "decay mode" is dependent upon the filament bias and we will suggest that surface mass migration is responsible for the "cooling" surge in exo-electron emission.

To demonstrate that exo-electron emission could be used to monitor the rate of reaction we measured (K) and  $I_e$  over a range of temperatures for the ammonia oxidation process. The data is shown in figure 6. The  $I_e$  curve follows the (K) curve until thermal emission begins to be significant, at that point  $I_e$  becomes very large. This almost linear relationship between (K) and  $I_e$  was observed with CO and  $H_2$  with different numerical values.

At this point we began to investigate the effects of external electric fields on catalysis and exo-electron emission. To avoid unnecessary discussion, we emphasize that from now on whenever a particular experimental effect is reported with CO,  $H_2$  or  $NH_3$ , the same experiment was repeated with the other two gases. If the results were qualitatively similar no further discussion is given. If there were significant differences, this is discussed in the text.

In the first electric field experiments we wished to see what effect, if any, would occur if we biased the catalyst to reduce or enhance exo-electron emission. For these experiments the catalyst was raised to its operating temperature ( $770^\circ C$ ) and then biased with the Fluke power supply to  $\pm 28$  volts. The first experiments indicated that changing the catalyst bias during a catalysis run did change the value of  $I_e$ . However, the value of (K) was unaffected. This suggested that exo-electron emission was related to surface migration during the catalytic induction phase, but that there was no direct connection between electron emission and catalysis itself.

This idea was found to be incorrect when we tried applying the bias voltage to the filament before heating it to begin catalysis.

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This is shown in figure 7 for oxidation of CO, a -28 volt bias increased both (K) and  $I_e$  over the no-bias values which are not shown to avoid confusing the figure. Conversely, a +28 volt bias decreased both (K) and  $I_e$  below the "no-bias" values. More detailed data on the effects of changing filament bias is shown in figure 8 for CO oxidation. Here the bias was changed each time the filament was cooled to 20°C. Then the catalyst was heated to 770°C again and held at that temperature until (K) was effectively constant. At this time the heating current was removed and the filament cooled to 20°C.

As we expected, the higher negative voltages yielded higher (K) values. More surprising is the way in which (K) rises (upon heating) and falls (upon cooling). At high voltages (-83V) the rise is rapid and the drop is preceded by a steep pulse which dies away very rapidly. At (-30V) the rise occurs much more slowly and the decay is significantly longer. There seems to be some sort of surface change which depends upon the filament voltage both in absolute value and in the rate of approach to equilibrium.

A similar experiment at a series of positive filament bias voltages indicated that +28 volts reduces both  $I_e$  and (K). Increasing the filament bias in steps to +80 volts reduced  $I_e$  to almost zero but had no effect on (K). Apparently the effect of a positive filament bias on the rate of catalysis (K) is complete at +28 volts. In contrast, (K) increases with negative filament bias up to about -100 volts.

There is direct evidence that a positive filament bias not only

reduces (K) but it can condition the filament against catalysis. Evidence of this effect is shown in figure 9. Here we have plotted (K) versus time (oxidation of CO) for a filament that was first biased at +30 volts to retard exo-electron emission. The filament was then cooled to 20°C and -30V was applied. An increased value of (K) was observed but it was significantly lower than that usually observed at -30V. We suspected that the +30V exposure had somehow "formed" the catalyst into an ineffective state. The catalyst was heated to 950°C in vacuum without any applied potential, then cooled to 20°C. The -30V was reapplied and the catalytic run repeated. The value of (K) was that normally observed with -30V potential suggesting that the +30V potential had "formed" the catalyst and the heating at 950°C had "annealed" the material.

One study was done to determine if the emitted exo-electron current had a complex energy spectrum. If such a spectrum existed it might be related to the presence of "activated complexes" as reaction intermediates. For this experiment the catalytic oxidation reaction was allowed to stabilize with the filament held at ground potential, then the filament voltage was raised in steps to +33V. The exo-electron current decreased each time the voltage increased. No structure in the  $I_e$  versus voltage curve was observed. This suggests that no reaction intermediates are involved in the exo-electron emission.

### III. Discussion and Conclusions

It seems quite clear that exo-electron emission may be used as a measure of the rate of certain catalytic reactions. The induction



phase and the approach to steady state can be observed without ambiguity in terms of exo-electron emission. The change in electron emission and rate of catalysis with electric fields indicates that catalysis can be partially controlled by external electric potentials.

The mechanism for these phenomena is not entirely clear at this time. We suggest that the large values of (K) and  $I_e$  observed during the induction period are due to mass migration of the catalyst material itself. Effects of this type are well known (10) and catalysts are often observed to be grooved and twisted after long use.

The steady state exo-electron emission is proportionate to the rate of catalysis itself and may be due to the adsorption step in the reaction. Delchar (11) has reported the emission of exo-electrons during chemisorption of oxygen on nickel, but the emission rate decayed rapidly as the surface became saturated. We see a steady state level indicating continuous adsorption and desorption which would, of course, be necessary for a continuous catalytic reaction.

The surge observed when the catalyst is allowed to cool may be due to relaxation of the "active" surface state that exists during catalysis. Effects of this type have been observed in silver thermal faceting experiments (12). The thermal facets developed at 865°C were observed to disappear as the temperature was raised and reappear as it was allowed to cool again. The extensive surface migration required to effect this change would induce copious exo-electron emission.

The fact that electric fields only affect catalysis if applied before the catalyst is heated, is somewhat surprising. Here we suggest that during the induction phase the catalyst surface is undergoing rearrangement to the state in which it is "active" for catalysis. During this period the surface arrangement can be affected by external electric fields. Effects of this type have been reported for thin films (13). In that study the electric field was applied during deposition and was shown to produce enhanced orientation of the deposited film. The electric field was only effective during deposition. If the field was applied to the completed film, no effect was noticed. We must emphasize that the parallelism here is not exact. The material used in (13) was Ag or Au, and the field was in the plane of the film rather than perpendicular to it. This experiment is cited as an example of the effect of an electric field during the induction period when the film is moving toward an equilibrium configuration. Similar effects on a catalyst surface may be the explanation of our observations of the effect of electric fields.

The electric field effects of reference (8) may have been due to the application of the field before the catalyst was heated (the text does not indicate how this was done). An increase in reaction rate, for oxidation of isopropyl alcohol over silver at 476°C, was observed with a negative bias on the catalyst. This is in agreement with the results reported above.

The data reported by reference (9) was taken with AC voltages over a wide range of frequencies. The data indicated that enhancement

of catalysis depended in a complex way upon both signal frequency and amplitude. The authors (8) suggested that the applied field might have induced excess electron emission from the catalyst. This would agree with our exo-electron results above. The other investigator (9B) suggested that enhancement of the rate of catalysis was observed when the applied signal frequency corresponded to the rate at which the sequence of adsorption, reaction and desorption occurred. We cannot comment upon this suggestion.

Future studies of catalysis will involve following mass migration of the catalyst surface with an optical microscope and using a soft X-ray system to monitor surface impurities.

Acknowledgments

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